Aerosol Precursor and Aerosol Instrumentation:

Field Measurements and Method Development

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Field Measurements:

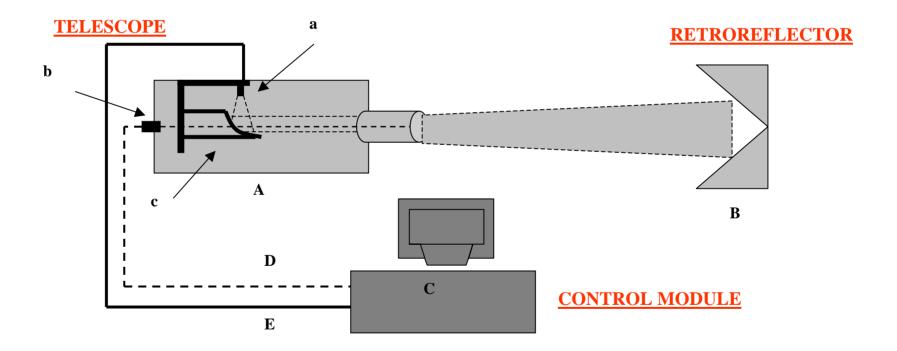
Selected instrumentation aimed at determining the amounts of scattering and absorbing aerosols as well as their precursors will be deployed at ground-based ASP field sites during ASP field efforts and the data obtained will be made available to the ASP community.

Focused Laboratory Studies:

To identify and quantitate highly colored organic carbonaceous aerosol components known as "humic-like" substances and to determine their effects on the radiative properties of carbonaceous aerosols.

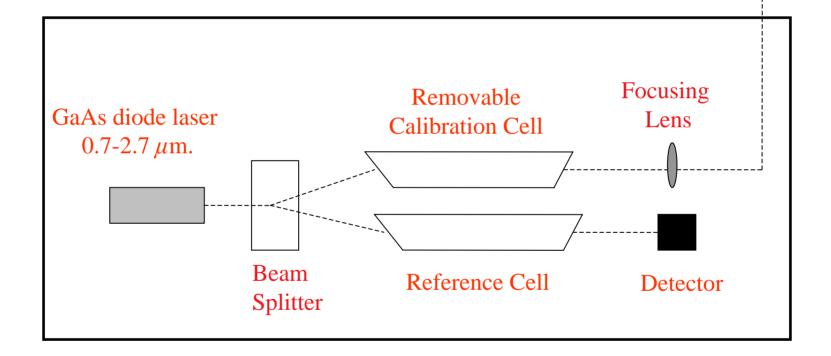
<u>Aerosol Precursors – Tunable Diode Laser Spectroscopy</u>

Ammonia – Near IR Open Path Absorption System



CONTROL MODULE

Fiber Optic



Estimated detection limits and line characteristics for measurement of ammonia with the NIRTDL system.

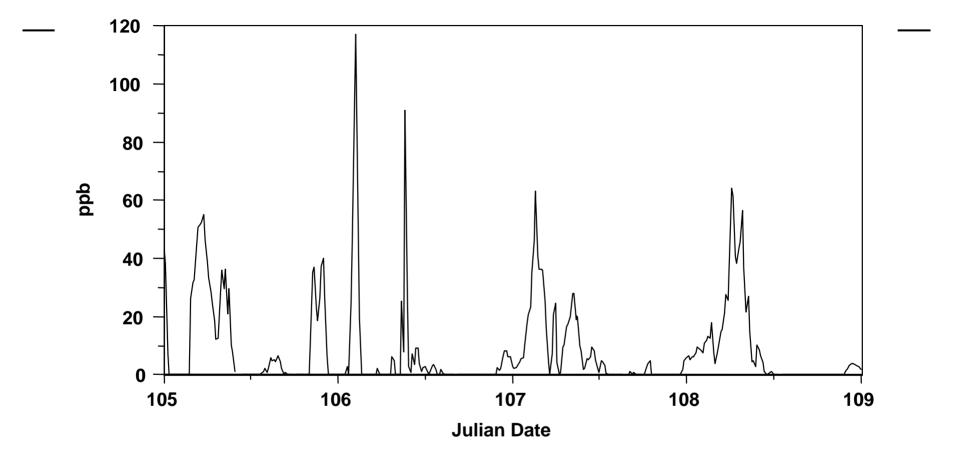
Parameter	Unit	Value
Wave number	cm ⁻¹	6478
Wavelength	μ m	1.544
Line strength	cm-molecule-1	3.7 x 10 ⁻²²
Line width	cm ⁻¹	0.060
Detection limit	ppm-m	0.203

Gives a detection limit of ~ 0.8 ppb for a path length of 244 m or ~ 0.2 ppb for a 1km path.





Ammonia measurements obtained in Mexico City - April 15-19, 2003. Path Length- 244 m.



A comparison with nephelometry and single particle mass spectrometry showed anti-correlation. Ammonia was seen primarily early in the day.

During midday to early afternoon, when photochemical activity leads to the production of nitric acid, the Titration of ammonia with nitric acid was observed to yield ammonium nitrate, depleting the ammonia in the air.





Application of the NIR-TDLAS instrumentation to other aerosol precursors with available tunable diode lasers

The Telescope/Retroreflector System is equipped for multiple lasers – multiple analytes.

Nitric acid:

A strong absorption band at 3552 cm⁻¹ (2.8 micron) with an integrated intensity of 2.82 X 10⁻¹⁹ cm/molecule and a weaker band at about 4850 (2.1 micron) with an integrated absorption intensity of 2 X 10⁻¹⁹ cm/molecule.

Other species of interest are hydrogen peroxide (H_2O_2) and sulfur dioxide (SO_2) .

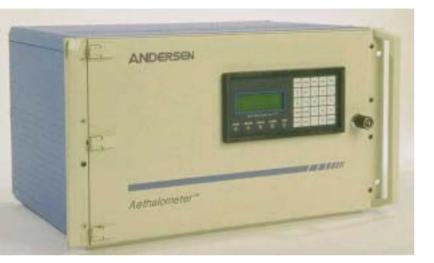
The use of multiple reflectors would allow for measurement of vertical profiles.





Aerosol Absorption and Black Carbon Measurements

7-channel aethalometer:



 $\lambda = 370, 470, 520, 590, 660, 880, and 950 nm.$

2-5 minute time resolution

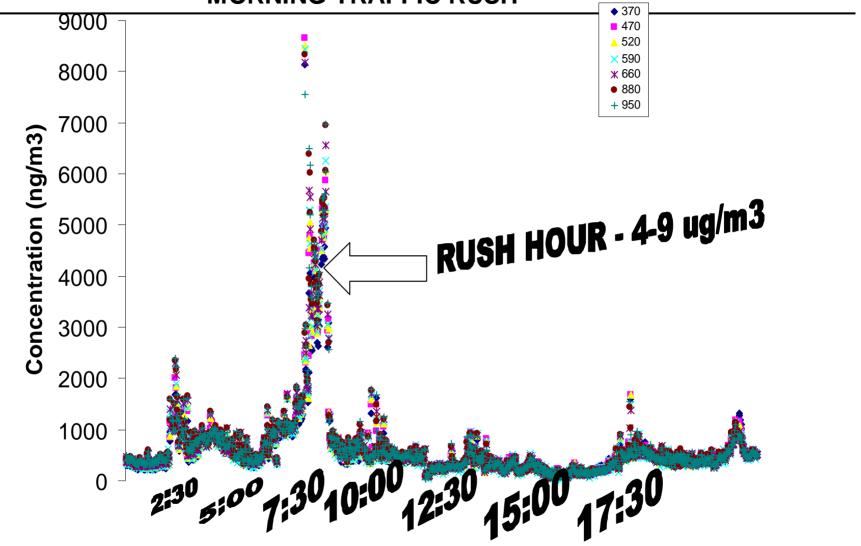
1-minute time resolution for single channel



Aerosol sample collected on a quartz fiber filter tape

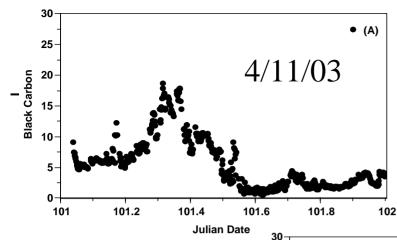
Amount of optically absorbing material per unit volume of sampled measured by transmission

BLACK CARBON - WED., AUG. 1, 2001, SHOWING MORNING TRAFFIC RUSH









MEXICO CITY – CENICA

880nm Channel, 3 consecutive Fridays

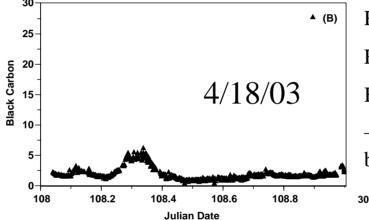
GOOD FRIDAY

Reduced BC consistant with

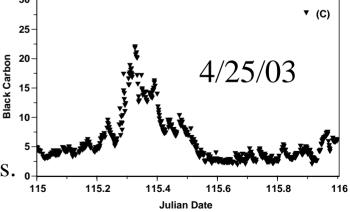
Reduced diesel traffic.

BC background level of $\sim 1 \,\mu \text{g/m}^3$

Biomass Burning, wood/trash burning

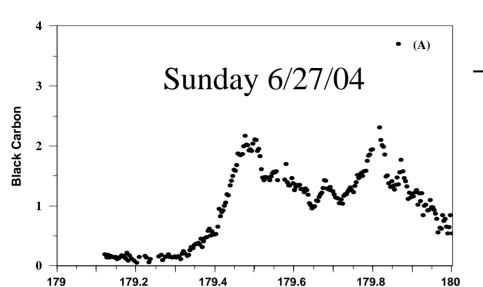


Other channels give similar results Indicating BC as the predominate absorbing species.

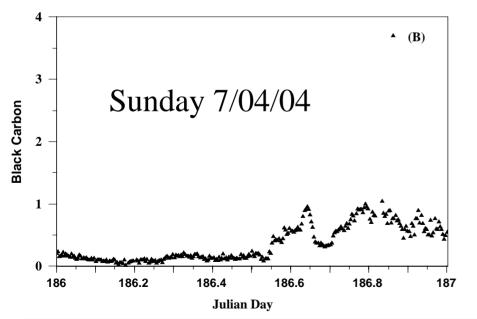








Julian Day



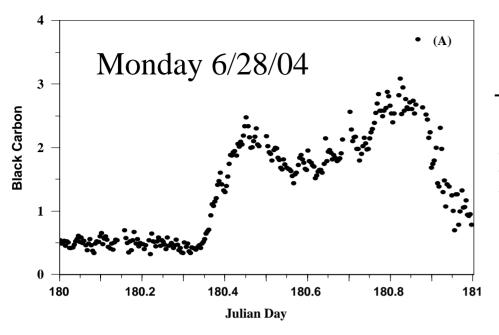
CHICAGO

10 Times Lower than Mexico City

General Traffic High – PARTY! BC low due to decreased heavy diesel

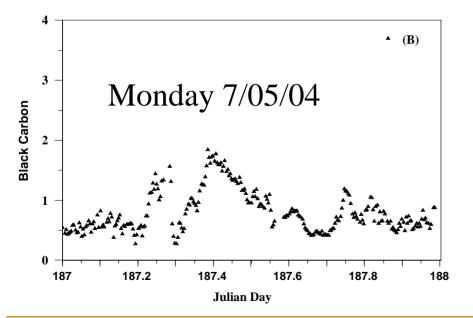






CHICAGO

Morning winds keep levels low until later in the AM



Diesel emissions increase on 7/5 over 7/4 Lower than that for a normal monday





Approach and Methods

- Aethalometer Results amount of BC aerosol (μ g/m³).
- Automatically calculated assuming a mass specific absorption coefficient for BC (19 m²/g).
- Field results will be recorded as total aerosol absorption as a function of wavelength $[\sigma_a(\lambda)(m^{-1})]$.
- A random selection of tape samples will be measured in the laboratory for BC content by a thermal evolution method.
- Absorption coefficient for BC aerosols can be calculated for each site from these measurements
- Direct Measurements of aerosol optical constants.
- The variation of the aerosol absorption strengths will be an indication of the types of BC aerosols present.
- Laboratory Calibration with known aerosols.
- Incorporation of integration sphere surrounding the detector assembly to minimize scattering losses.





OTHER MEASUREMENTS

<u>Three wavelength nephelometer</u> - fine aerosol particle scattering.

Mid-IR TDLAS system - nitric acid as the precursor to nitrate aerosols.

Seven-channel visible multi-filter rotating band radiometer

Robertson-Berger broadband UV-B meter



"Humic-Like" Organic Absorbing Aerosols

Evaluate the amount of potentially absorbing organic aerosols associated with BC that may enhance aerosol absorption at shorter wavelengths and also to determine the amount of water soluble absorbing species found in precipitation samples which may act to increase absorption in clouds.

Aerosol samples collected at on glass fiber filters and in precipitation samples

Water-soluble species - water washing

Insoluble fraction separated into BC & OC - rapid heating of the samples to 400 C in a helium atmosphere

Absorption of the aerosols as a function of wavelength to evaluate the contributions of both water-soluble species and OC to the total aerosol absorption.

Aqueous fractions - hollow-fiber ultrafiltration (<1000 – 30,000 MW)

Functional Group Analysis – FTIR CIR





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